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EXPERIMENTAL STUDIES OF THE FORMATION/DEPOSITION

OF SODIUM SULFATE IN/FROM COMBUSTION GASES

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FIGURES

1. INTRODUCTION AND RESEARCH OBJECTIVES

Gas turbine development is being impeded by performance losses and "hot corrosion" of components resulting from the deposition of inorganic salts (e.g., Na_2SO_4) and oxides present in the combustion products. Engine operating experience and captive engine tests have provided valuable clues to such phenomena, but smaller-scale laboratory experiments under more precisely controlled conditions, coupled with necessary advances in deposition rate theory, will be necessary to obtain an improved understanding of the mechanisms of deposition on which future control measures can be based.

To guide the required theoretical developments, it is essential that controlled experiments are carried out and immediately confronted with the best available theory; indeed, the experimental design itself should be carried on in the light of currently available theory.[1,2] Only in this way will it be possible to pinpoint the weak spots, and advance the theory in those areas of greatest practical significance. While data on operating engines is necessary and suggestive, definitive tests and necessary extensions of the theories outlined above will require laboratory experiments under well-instrumented, specifically selected conditions. Moreover, new experimental techniques will have to be developed,[3] some of which may be transferable to engine test conditions or even operational engines (as "on-line" detectors). In what follows we briefly indicate the nature and shortcomings of previously available experiments, and these give a brief account of experiments currently in progress [4-6] under NASA Grant NSG 3169. For further details, the reader is directed to References.

Most previous deposition rate information is the result of lengthy "batch" experiments in which the mass accumulated after hours of exposure is determined by weighing or equivalent chemical or physical analysis. Particularly relevant examples are the blade cascade experiments of Nomura, et al.[6] and the Na_2SO_4 deposition experiments of Kohl and Fryburg, et al.[4] and Laxton, et al.[5] Two particularly troublesome aspects of such experiments have been:

  i) the uncertain state of the free-stream (actual inorganic content and its detailed physical and/or chemical state);

  ii) the test duration required to obtain data of reasonable precision.

Since these factors have limited the yield and hence impact of such experiments, we have moved in the direction of configurations/techniques which lend themselves to better mainstream characterization and short-duration (on-line) optical measurement of deposition rates (and dew points). As an example, we cite below $B_2O_3(\ell)$ deposition rate data obtained interferometrically[7] and ellipsometrically[8] in seeded flame experiments of ca. 15 second duration.

2. RECENT ADVANCES IN THE OPTICAL MEASUREMENT OF WALL CONDENSATION RATES IN COMBUSTION SYSTEMS

2.1 Approach[3],[7],[8]

We have already demonstrated that remote optical methods can be used for measuring dew points, and deposition rates of inorganic salts on surfaces exposed to seeded combustion gases. Such measurements are made either by recording interference in a reflected beam of monochromatic light,[3],[7],[8] or by measuring the change in polarization upon reflection and passage through the transparent film (see below). To demonstrate these methods a deliberately simple experimental system is used, in which an electrically heated platinum ribbon is immersed in seeded flat-flame combustion product gases (see Figure 1). To avoid experimental uncertainties involved in accurately providing and measuring steady flow rates of salt solutions into the burner, boron trichloride, a gas at STP, is used as the seed material in these preliminary experiments. Boric oxide (B_2O_3) and its vapor precursors are formed in the flame and the B_2O_3 dew point and growth rate were successfully measured using a simple reflectance/interference technique Interestingly enough, in this system it appears that $HBO_2(g)$ is the dominant B-containing vapor species responsible for the observed growth, moreover, the observed dew points can only be explained if $(HBO_2)_3(g)$ does not form at the vapor/liquid interface.

2.2 Optical Arrangement for Polarization Measurements[8],[9]

A schematic of the optical arrangement used for ellipsometrically measuring the B_2O_3 growth rate on platinum ribbon surfaces, is shown in Figure 1. A helium-neon laser L (Spectra Physics Model 145P), with an output power level of 2mW, is the source of monochromatic light. To render the intensity of the light reaching the target approximately independent of polarizer angle, the beam is first circularly polarized by use of mica, quarter-wave plate, C_1 (12mm aperture, broadband coated, for 0.6328μm radiation) placed with its fast axis at the appropriate angle ahead of the laser. The circularly polarized light is then linearly polarized by use of a Glan-Thompson prism polarizer P (made of calcite, with an aperture-to-length ration of 8:25). The linearly polarized light is then elliptically polarized by use of a compensator C_2 (quartz, cemented quarter-wave plate, 14mm aperture, broadband coated, for 0.6328μm radiation), placed with its fast axis at 45° to the plane of incidence (resulting in equal amplitudes of the p and s components of the elliptically polarized beam incident on the surface.[9] To focus the incident beam onto the target a double convex lens L_1 was placed at a focal length distance from the target. The reflected beam from the target is then analyzed by use of a Glan-Thompson prism A (similar to P), placed ahead of the detector D. Two double convex lens L_3 and L_4 are used to focus the beam onto the photocell aperture of the detector. For high temperature application (>1000K) an interference filter I, which transmits only 0.6328μm light, was placed ahead of the detector to prevent light emitted by the target at other wavelengths from reaching the detector. The detector output is displayed on a strip chart recording potentiometer.[10] A pinhole was placed ahead of the collimating lenses L_2

and L_3 to minimize scattered light from the surface, and parasitic beams from the other optical components, from entering the detector. The quarter wave plates and the Glan-Thompson prisms were obtained from Karl Lambrecht Corporation, Chicago, Illinois. The compensator C_2 and the polarizer/analyzer unites P and A, were mounted on divided circle rotators permitting angular adjustments accurately to 6 min, and 1 min, respectively. The interference filter, and the lenses L_1, L_2, L_3 were checked and found to introduce negligible birefringence. In most cases, an increase in film thickness by one-half wavelength results in an azimuth change of a full turn. Under these conditions an angular resolution of 1 min results in an average resolution in film thickness of about 0.2A.

2.3 Results[8]

Ellipsometric results for the inferred deposition rate of boric oxide as a function of the platinum surface temperature are shown in Figure 2. The points represent the experimental measurements, and the curve was obtained based on theoretical calculations of the deposition rate of B_2O_3 expected under these conditions but matched to the data at 1200K (see references 1, 2, 7 for details of the theoretical estimates of multicomponent chemical vapor deposition rates). The observed agreement lends support to both the boundary layer transport theory and data reduction procedure. Measurements of the deposition rate of boric oxide using the interference method were made previously[3,7] under similar flow conditions. These measurements were also in excellent agreement with the polarization technique results reported herein, further supporting these new data.

Evaporation rates of boric oxide as a function of the ribbon surface temperature (rate data which we were unable to obtain previously using the interference method[7] have also been obtained. It thus appears that the polarization (ellipsometric) technique will allow measurements of both rapid net condensation and evaporation rates thereby opening the door to a more comprehensive test of multicomponent CVD theory under combustion conditions.

We are presently extending these optical techniques to measure Na_2SO_4 deposition, hopefully including mist-containing mainstreams. We also plan to develop a variant of the optical technique (based on light scattering from a dilute surface layer) to make on-line measurements of solid aerosol deposition on cooled and heated targets.

3. ADMINISTRATIVE INFORMATION

A manuscript describing our use of the polarization (ellipsometric) method to obtain dew points and deposition rates has been prepared and will be submitted next month for publication in Combustion and Flame.[8] We are also preparing a comprehensive account of our deposition theory and experiments for presentation at the 18th International Combustion Symposium[10] next summer.

The work described in the present report is primarily the result of the writer's collaboration with Dr. K. Seshadri, who completed his postdoctoral research here on 31 August 1979. This research will be continued and extended by Dr. Y. Ueno, who joined our research group on 1 July 1979.

During the period 1 October 1979 – 31 December 1979 the writer will be based at the Quantum Institute – UCal/Santa Barbara, in part to investigate the potential of laser induced fluorescence techniques for monitoring chemical changes in flat flame combustion product gases. In addition, laboraotry visits have been made to the University of New Hampshire (8/14/79; SiO_2 aerosol production in flames), Brigham Young University (9/24/79; pulverized coal combustion research), Stanford University (11/9/79; laser flame diagnostics), and U Cal/Berkeley (11/12/79; laser flame diagnostics).

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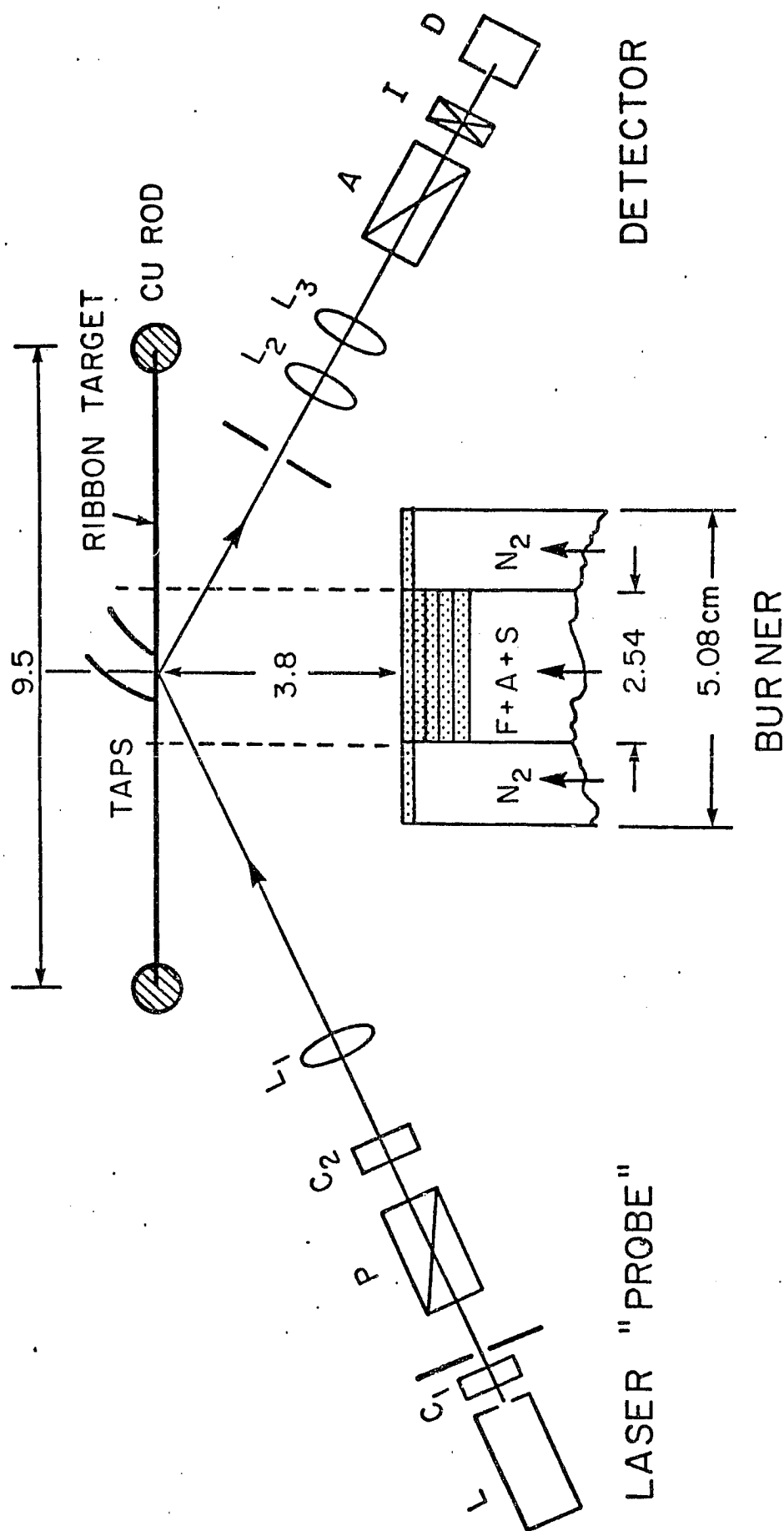
Figure 1: Optical (ellipsometric) arrangement for thin film growth and evaporation rate measurements;
L= Laser, C₁= 1/4 wave plate, P= polarizer, C₂= compensator, A= analyzer, I= filter, D= detector,
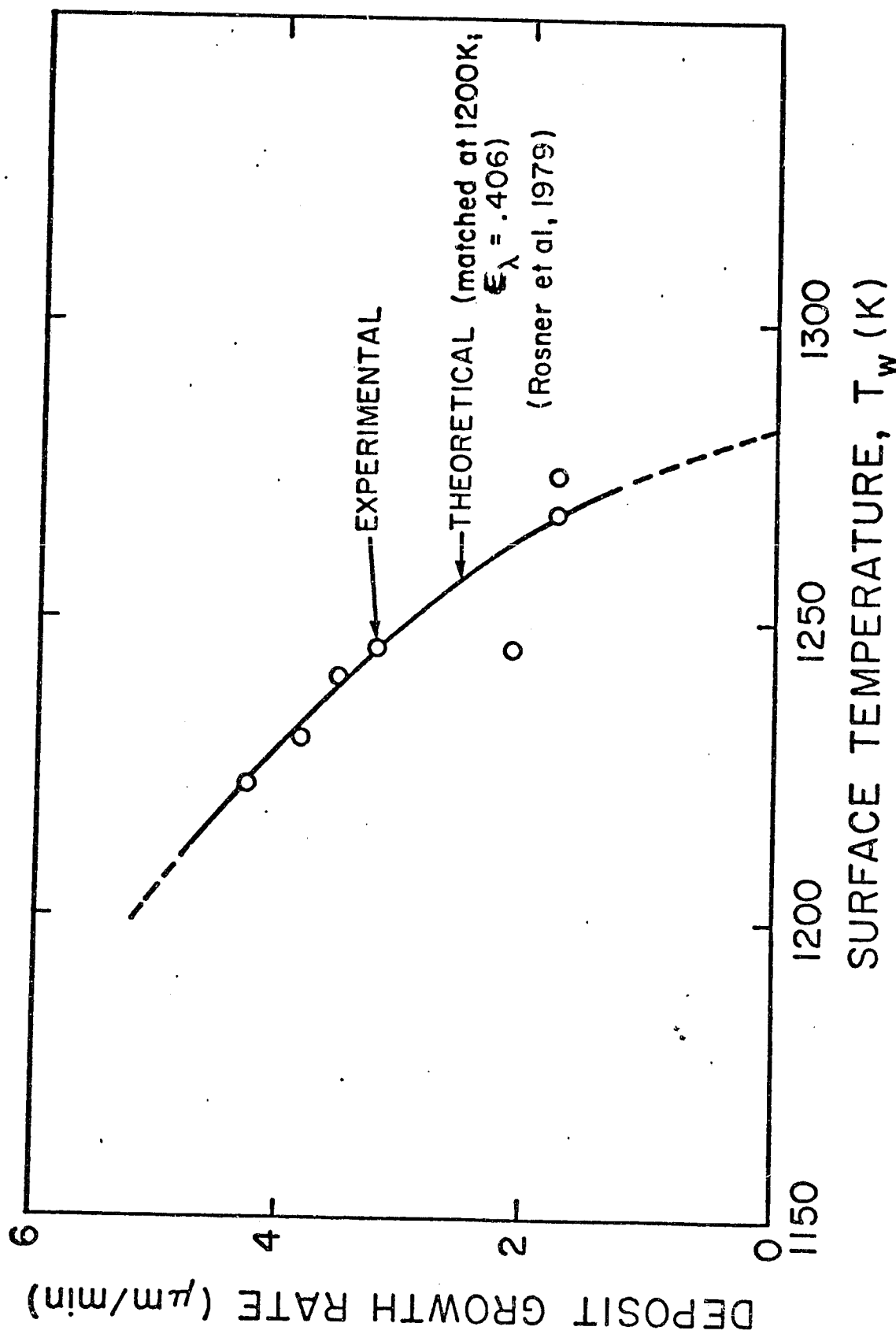L₁, L₂, L₃ = focussing lenses.

FIGURE 2: Experimentally measured (ellipsometric) and theoretical predictions of deposition rates of $B_2O_3(\ell)$; angle of incidence 70°, 2.23 moles of BCl_3 (as pct of fuel), $\phi = 0.78$, calculation of experimental rate based on peak width at half maximum, $D_{HBO_2} \cdot \overline{Nu}_m = 95 \ cm^2/sec$.

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16. Abstract

An optical polarization ("ellipsometric") technique is developed for measuring rapidly growing and evaporating transparent liquid condensate films (e.g., boric oxide) on solid surfaces exposed to combustion product gases. To demonstrate the validity of the technique our new polarization method results for the B_2O_3 deposition rate from BCl_3-seeded propane/air flames are shown to agree well with the results of our earlier interference measurements, and also with theoretical CVD predictions. While previously unable to interferometrically measure $B_2O_3(\ell)$ evaporation rates these rates (from platinum ribbons into seeded propane air flames) are here estimated using the polarization technique. It appears that, compared with the interference method, the polarization technique places less stringent requirements on surface quality, which may justify the added optical components needed for such measurements. We conclude that the complementary optical methods of polarization (ellipsometry) and interference hold considerable promise for application to the rapid measurement of condensation and evaporation rates in high temperature (e.g., combustion product) environments.

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